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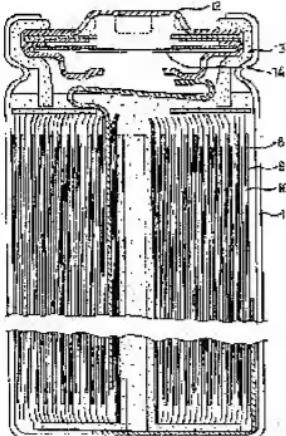
(72)Inventor : INOUE HIROSHI
YASUNAMI SHOICHIRO
INOUE AKIYUKI

(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To improve productivity of a highly safe nonaqueous secondary battery provided with a high discharge voltage and an excellent charge-discharge cycle characteristic by forming a specific protecting layer on a negative electrode and/or a positive electrode.

SOLUTION: A nonaqueous secondary battery is constructed of a positive electrode and a negative electrode, which contain materials plastically storing/releasing lithium, a nonaqueous electrolyte containing lithium salt, and a separator, and in the negative electrode and/or the positive electrode, at least one protecting layer formed of solid particles and a water soluble polymer is formed. In the protecting layer, conductive particles may be contained in addition to the solid particles and the water soluble polymer. The thickness of the protecting layer is 1-40 μ m desirably. An inorganic chalcogenide particle is feasible for the solid particle contained in the protecting layer. A polyacrylic derivative or a cellulose derivative is feasible for the water soluble polymer. For the conductive particle, a carbonaceous compound, natural graphite, and vapor phase growth carbon are desirable in particular.



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2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention relates to the nonaqueous secondary battery which raised productivity and which is excellent in a life and safety with high discharge potential.

[0002]

[Description of the Prior Art] The protective layer which becomes JP,61-7577,A from the substance having electronic conductivity and ion conductivity, such as lithium, about the surface of an anode is indicated, and it is indicated that the oxide of tungsten, molybdenum, and vanadium is preferred as a substance which has electronic-ion mixing conductivity. However, these compounds have not come to show sufficient effect of preventing an internal short circuit. To JP,4-28173,A, installing the poly membrane which penetrates this alkali metal ion selectively on an anode and the negative-electrode (alkaline metal or alkaline metal alloy) side which counters is indicated. However, installation of these porous poly membranes has conceived the problem on which cell capacity is reduced substantially.

[0003]

[Problem(s) to be Solved by the Invention] Therefore, the technical problem of this invention is raising the productivity of the nonaqueous secondary battery which had high discharge voltage and a good charge-discharge cycle characteristic, and also was excellent in safety.

[0004]

[Means for Solving the Problem] An anode and a negative electrode in which a technical problem of this invention includes for lithium material in which occlusion discharge is possible reversibly, In nonaqueous electrolyte containing lithium salt and a nonaqueous secondary battery which comprises a separator, this negative electrode and/or an anode have at least one layer of protective layers, and it was attained by nonaqueous secondary battery becoming if these protective layers are a particle and water-soluble polymer.

[0005]

[Embodiment of the Invention] The anode and negative electrode which include reversibly the material in which occlusion discharge is possible for lithium, this invention persons, The place which examined wholeheartedly the bad cause of the manufacture yield of the nonaqueous electrolyte containing lithium salt and the nonaqueous secondary battery which comprises a separator, Unevenness of the protuberance form of an electrode surface, the crack of the electrode surface produced from conveyance of an electrode to a battery assembly in process, When become a cause and a separator is directly destroyed at the time of cell winding, or unevenness by partial omission etc. is connected with delicate sliding at the time of winding and the unevenness of a pressure and destroys a separator showed that contribution of the internal short circuit having occurred was large. In order to prevent a part short circuit among these, it was effective in the electrode surface to provide a protective layer, and installation of the protective layer raised the manufacture yield, and it turned out that safety is also raised. It turned out that the above can be attained without being accompanied by the fall of service capacity, especially the service capacity in high electric current because a protective layer does not contain a resin binding agent but contains water-soluble polymer.

[0006] Although the desirable mode of this invention is shown below, this invention is not limited to these.

- (1) The anode and negative electrode which include for lithium the material in which occlusion discharge is possible reversibly, The nonaqueous secondary battery this negative electrode and/or an anode having at least one layer of protective layers, and becoming in the nonaqueous electrolyte containing lithium salt and the nonaqueous secondary battery which comprises a separator if these protective layers are a particle and water-soluble polymer.
- (2) The anode and negative electrode which include for lithium the material in which occlusion discharge is possible reversibly, A nonaqueous secondary battery, wherein this negative electrode and/or an anode have at least one layer of protective layers and this protective layer consists of a particle, a conductive particle, and water-soluble polymer in the nonaqueous electrolyte containing lithium salt and the nonaqueous secondary battery which comprises a separator.
- (3) (1), wherein the thickness of this protective layer is 1 micrometers or more 40 micrometers or less Or (2) Nonaqueous secondary battery of a statement.
- (4) (3), wherein this protective layer is formed on a negative electrode Nonaqueous secondary battery of a statement.
- (5) (3), wherein this protective layer is formed on an anode Nonaqueous secondary battery of a statement.
- (6) (3), wherein this protective layer is formed in both on an anode and a negative electrode Nonaqueous secondary battery of a statement.

(7) (3), wherein this protective layer does not contain a conductive particle on an anode but contains a conductive particle on a negative electrode Nonaqueous secondary battery of a statement.

(8) (4) to (7), wherein the particles contained in this protective layer are inorganic chalcogenide particles Nonaqueous secondary battery given in any 1 paragraph.

(9) (8), wherein these inorganic chalcogenide particles contain at least one sort of oxides of sodium, potassium, magnesium, calcium, strontium, a zirconium, aluminum, and silicon Nonaqueous secondary battery of a statement.

(10) (9), wherein the oxides of (9) are alumina, a silicon dioxide, and zirconia Nonaqueous secondary battery of a statement.

(11) (8), wherein the water-soluble polymer contained in a protective layer is a polyacrylic acid derivative or a cellulosic from -- nonaqueous secondary battery given in any 1 paragraph of (10). (12) A nonaqueous secondary battery given in (11), wherein the conductive particle contained in a protective layer is a carbon material.

(13) A nonaqueous secondary battery given in (12), wherein the negative pole material in which occlusion discharge is possible uses lithium as a metallic oxide reversibly.

(14) A nonaqueous secondary battery given in (13), wherein this negative electrode is a multiple oxide containing tin.

(15) A nonaqueous secondary battery given in (14), wherein the multiple oxide containing this tin is a multiple oxide of the following general formula (1).



Among a formula, M^1 expresses two or more sorts of elements chosen from aluminum, B, P, Si, the 1st group element of the periodic table, the 2nd group element, the 3rd group element, and a halogen, a expresses 0.2 [or more / 2] or less numbers, and t expresses or more 1 six or less number.

(16) A nonaqueous secondary battery given in (15), wherein the multiple oxide containing this tin is a multiple oxide of the following general formula (2).



As for M^2 , M^3 among a formula at least two sorts of aluminum, B, P, and Si The 1st group element of the periodic table, Expressing at least one sort of the 2nd group element, the 3rd group element, and a halogen, b is 0.2 [or more / 2] or less numbers, c is or more 0.01 one or less number, and $0.2 < b+c < 2$ and t express or more 1 six or less number.

(17) (1), wherein this negative electrode is electrically connected to metal lithium from -- nonaqueous secondary battery given in (16).

[0007]In this invention, a protective layer consists of at least one layer, and may be constituted by congener or two or more layers of a different kind. As for the thickness of a protective layer,

1 micrometers or more 40 micrometers or less are preferred, and it is not less than 2 micrometers 30 micrometers or less more preferably. It dissolves below 300 ** or, as for the protective layer containing these particles, what does not form a new coat is desirable. These protective layers may contain an organic or inorganic particle without conductivity, and may also contain it in accordance with the particle of conductive organicity or inorganic matter. An inorganic particle is more preferred among these particles.

[0008]As inorganic substance particles, metal, the carbide of a nonmetallic element, silicide, a nitride, a sulfide, and an oxide can be mentioned. In carbide, silicide, and a nitride, SiC, aluminium nitride (AlN), BN, and BP have highly and chemically stable insulation, and are preferred, and especially SiC using especially BeO, Be, and BN as a sintering auxiliary agent is preferred. In chalcogenide, an oxide is preferred and the oxide which oxidizes or is hard to be returned is preferred. As these oxides, aluminum₂O₃, As₄O₆, B₂O₃, BaO, BeO, CaO, Li₂O, K₂O, Na₂O, In₂O₃, MgO, Sb₂O₅, SiO₂, SrO, and ZrO₂ are raised. In these, aluminum₂O₃, BaO, BeO, CaO, K₂O, Na₂O, MgO, SiO₂, SrO, and especially ZrO₂ are preferred. These oxides may be independent or may be multiple oxides. As a compound desirable as a multiple oxide, mullite (3aluminum₂O₃ and 2SiO₂), A steatite (MgO-SiO₂), forsterite (2 MgO-SiO₂), cordierite (2MgO, 2aluminum₂O₃, and 5SiO₂), etc. can be mentioned. As a conductive particle, inorganic particles are preferred and the particles of a metal powder, inorganic chalcogenide, and a carbonaceous compound are mentioned. In particular, a carbonaceous compound, natural graphite, and vapor-phase-epitaxy carbon are preferred.

[0009]By methods, such as control of a generation condition, and grinding, 0.1 micrometers or more 20 micrometers or less, preferably, these inorganic compound particles are made into 0.2-micrometer or more a particle of 15 micrometers or less, and are used especially.

[0010]the content of particles used for this invention -- 1 - 80 g/m² -- it is 2 - 40 g/m² preferably. A protective layer is formed from the particle and water-soluble polymer which do not mainly have conductivity substantially [above], or the particle, the conductive particle and water-soluble polymer which do not have conductivity substantially. 96 or less % of the weight of 40 % of the weight or more has preferred particles to both gross weight, and, as for the ratio of a particle and water-soluble polymer, 92 or less % of the weight of 50 % of the weight or more is more preferred. As water-soluble polymer, there are cellulosics, such as carboxymethyl cellulose and hydroxyethyl cellulose, a polyacrylic acid derivative, a polyvinyl alcohol derivative, a polyethylene oxide derivative, starch, etc., and a cellulosic and a polyacrylic acid derivative are preferred.

[0011]A protective layer may be painted on either one of an anode or a negative electrode, or may be painted on both an anode and a negative electrode. When an anode and a negative

electrode paint a mixture on the both sides of a charge collector and are formed in them, a protective layer may be a gestalt which may be painted on the both sides and painted only on one side. However, it needs to be painted on either one of [which opposes via a separator] an anode or a negative electrode. After the painting method of a protective layer paints the mixture which includes for lithium the material in which occlusion discharge is possible reversibly on a charge collector, the serial method which paints a protective layer one by one may be sufficient as it, and it may be a simultaneous coating method which paints a binder layer and a protective layer simultaneously.

[0012]Positive and the negative electrode which are used for the nonaqueous secondary battery of this invention can paint positive electrode mixture or negative electrode mixture on a charge collector, and can make it. A conducting agent, a binder, a dispersing agent, a filler, an ion conducting agent, a pressure enhancement agent, and various additive agents can be included in an anode or negative electrode mixture at each besides positive active material or a negative pole material, respectively.

[0013]As a negative pole material used by this invention, what is necessary is just a compound which can carry out occlusion discharge of the light metal ion. Although there are a light metal, a light metal alloy, a carbonaceous compound, an inorganic oxide, inorganic chalcogenide, a metal complex, and an organic polymer compound in these, a carbonaceous compound, an inorganic oxide, and inorganic chalcogenide are preferred. These may use in combination. For example, the combination of a light metal, a carbonaceous compound and a light metal, an inorganic oxide and a light metal, a carbonaceous compound, and an inorganic oxide, etc. are mentioned. Since these negative pole materials give the effect of high capacity, high discharge potential, high safety, and high cycle nature, they are preferred. As light metal ion, lithium is preferred.

[0014]What is chosen from natural graphite, an artificial graphite, vapor-phase-epitaxy carbon, the carbon in which the organic matter was calcinated, etc. as a carbonaceous compound, and includes black lead structure is preferred. A different-species compound, for example, B, P, N, S, SiC, and B4C may also be included in a carbonaceous compound zero to 10% of the weight besides carbon.

[0015]As an element in which ***** forms chalcogenide, ***** has the periodic table 13 to 15 fellows' metal, and preferred metalloid element. Especially as a transition metal compound, V, Ti, Fe, Mn, Co, nickel, Zn, W, and Mo are independent, or a multiple oxide or chalcogenide is preferred. As a desirable compound, $Li_pCo_qV_{1-q}O_r$ (it is $p=0.1-2.5$, $q=0-1$, and $z=1.3-4.5$ here) given in JP,6-44,972,A can be mentioned.

[0016]As a compound of metal other than a transition metal, and semimetal, the oxide of the element of the 13th fellows of the periodic table - 15 fellows, Ga, Si, Sn, germanium, Pb, Sb, and Bi which is independent or consists of two or more sorts of those combination, and

chalcogenide are chosen. For example, Ga_2O_3 , SiO , GeO , GeO_2 , SnO , SnO_2 , SnSiO_3 , PbO , PbO_2 , Pb_2O_3 , Pb_2O_4 , Pb_3O_4 , Sb_2O_3 , Sb_2O_4 , Sb_2O_5 , Bi_2O_3 , Bi_2O_4 , Bi_2O_5 , SnSiO_3 , GeS_2 , SnS , SnS_2 , PbS , PbS_2 , and Sb_2S_3 , Sb_2S_5 , SnSiS_3 , etc. are preferred. These may be a multiple oxide with lithium oxide, for example, Li_2GeO_3 , and Li_2SnO_2 .

[0017] As for the above-mentioned compound chalcogen compound and a multiple oxide, it is preferred that it is mainly amorphous at the time of cell inclusion. That it is amorphous is a thing which has a broadcloth dispersion belt which has the peak from 20 degrees to 40 degrees with 2theta value with the X-ray diffraction method using CuK alpha rays said here, and it may mainly have a crystalline diffraction line. Among the crystalline diffraction lines preferably looked at by not less than 40 degrees 70 degrees or less with 2theta value, the strongest intensity, it is 100 or less times that they are 500 or less times of the diffraction line intensity of the peak of the broadcloth dispersion belt looked at by not less than 20 degrees 40 degrees or less with 2theta value desirable still more preferably, and they are 5 or less times especially preferably -- most -- desirable -- It is not having a crystalline diffraction line.

[0018] The above-mentioned compound chalcogen compound and a multiple oxide are a compound chalcogen compound of three or more sorts of elements in B, aluminum, Ga, In, Ti, Si, germanium, Sn, Pb, P, As, Sb, and Bi, and a multiple oxide, and are a multiple oxide more preferably. It is a multiple oxide which comprises B, aluminum, Si, germanium, Sn, and three or more sorts of elements in P preferably especially. Since amorphous structure is mainly embellished, these multiple oxides may also contain the periodic table's element or halogen of one to three fellows.

[0019] In the above-mentioned negative pole material, especially the amorphous multiple oxide that makes tin a subject is preferred, and it is expressed with the following general formula (1).

SnM_a^1O_t general formula (1)

Among a formula, M^1 expresses two or more sorts of elements chosen from aluminum, B, P, Si, the 1st group element of the periodic table, the 2nd group element, the 3rd group element, and a halogen, a expresses 0.2 [or more / 2] or less numbers, and t expresses or more 1 six or less number.

[0020] In a general formula (1), the compound of the following general formula (2) is still more preferred.

SnM_b^2O_t general formula (2)

Among a formula, M^2 expresses two or more sorts of elements chosen from aluminum, B, P, the 1st group element of the periodic table, the 2nd group element, the 3rd group element, and a halogen, b expresses 0.2 [or more / 2] or less numbers, and t expresses or more 1 six or

less number.

[0021]In a general formula (1), the compound of the following general formula (3) is still more preferred.



As for M^3 , M^4 among a formula at least two sorts of aluminum, B, P, and Si The 1st group element of the periodic table, Expressing at least one sort of the 2nd group element, the 3rd group element, and a halogen, c is 0.2 [or more / 2] or less numbers, d is or more 0.01 one or less number, and $0.2 < c+d < 2$ and t express or more 1 six or less number. It is an element for making the compound of a general formula (3) make it amorphous as a whole, M^3 is an element in which un-crystallizing is possible, and, as for M^3 and M^4 , it is preferred to use combining two or more sorts of aluminum, B, P, and Si. M^4 is an element in which amorphous ornamentation is possible, and is the 1st group element of the periodic table, the 2nd group element, the 3rd group element, and a halogen, and K, Na, Cs, Mg, Ca, Ba, Y, and F are preferred. b is 0.2 [or more / 2] or less numbers, c is or more 0.01 one or less number, and $0.2 < b+c < 2$ and t express or more 1 six or less number.

[0022]Although the calcinating method and any method of a solution technique can be used for the amorphous multiple oxide of this invention, its calcinating method is more preferred. After mixing well the oxide or compound of an element indicated to the general formula (1) in the calcinating method, it is preferred to calcinate and to obtain an amorphous multiple oxide.

[0023]As a firing condition, it is preferred that it is a not less than 5 **/m heating rate of 200 ** or less as a heating rate, it is preferred as calcination temperature that it is [not less than 500 **] 1500 ** or less, and it is preferred that it is 100 or less hours as firing time for 1 hour or more. And it is preferred that it is below not less than $2 **/m 10^7 **$ as a lower temperature falling speed. The heating rate in this invention is the mean velocity of a rise in heat until it reaches "80% of calcination temperature (** display)" from "50% of calcination temperature (** display)". The temperature falling speed in this invention is the mean velocity of a temperature reduction until it reaches "50% of calcination temperature (** display)" from "80% of calcination temperature (** display)." It may cool all over a firing furnace and a temperature fall is taken out outside a firing furnace again, for example, may be supplied underwater and may be cooled. the gun method and the Hammer-Anvil method given in 217 pages of ceramic processing (Gihodo Shuppan 1987) -- rapid quenching, such as the -slap method, a gas atomizing method, the plasma-spraying method, a centrifugal quenching method, and the melt drag method, can also be used. It may cool using the single roller method given in 172 pages of new glass handbooks (Maruzen 1991), and the congruence roller method. In the case of the material fused during calcination, fired material may be taken out continuously, supplying a raw

material during calcination. It is preferred to stir melt in the case of the material fused during calcination.

[0024]Oxygen content is the atmosphere below 5 volume % preferably, and a calcination gas atmosphere is an inert gas atmosphere still more preferably. Nitrogen, argon, helium, krypton, a xenon, etc. are mentioned as inactive gas. The most desirable inactive gas is pure argon.

[0025]As for the mean grain size of the compound shown by this invention, 0.1-60 micrometers is preferred. In order to use predetermined grain size, the grinder and classifier which were known well are used. For example, a mortar, a ball mill, a sand mill, a vibration ball mill, a satellite ball mill, a planetary ball mill, a turning air stream type jet mill, a screen, etc. are used. The wet milling which made organic solvents, such as water or methanol, live together at the time of grinding can also be performed if needed. It is preferred to perform a classification, in order to consider it as desired particle diameter. As the classification method, there is no limitation in particular and a screen, a pneumatic elutriation machine, etc. can be used if needed. Dry type and a wet type can use a classification.

[0026]Although the example of the negative pole material of this invention is shown below, this invention is not limited to these. $\text{SnB}_{0.5}\text{P}_{0.5}\text{O}_3$, $\text{SnAl}_{0.3}\text{B}_{0.5}\text{P}_{0.2}\text{O}_{2.7}$, $\text{SnAl}_{0.3}\text{B}_{0.7}\text{O}_{2.5}$,

$\text{SnSi}_{0.8}\text{P}_{0.2}\text{O}_{3.1}$, $\text{SnSi}_{0.8}\text{B}_{0.2}\text{O}_{2.9}$, $\text{SnSi}_{0.8}\text{aluminum}_{0.2}\text{O}_{2.9}$, $\text{SnSi}_{0.6}\text{aluminum}_{0.2}\text{B}_{0.2}\text{O}_{2.8}$ and

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$\text{SnSi}_{0.8}\text{aluminum}_{0.3}\text{B}_{0.2}\text{P}_{0.2}\text{O}_{3.85}$, $\text{SnAl}_{0.1}\text{B}_{0.5}\text{P}_{0.5}\text{Mg}_{0.1}\text{F}_{0.2}\text{O}_{3.15}$ [0027] $\text{SnSi}_{0.8}\text{Mg}_{0.2}\text{O}_{2.8}$,

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[0028] $\text{Sn}_{0.9}\text{Mn}_{0.3}\text{B}_{0.4}\text{P}_{0.4}\text{Ca}_{0.1}\text{Rb}_{0.1}\text{O}_{2.95}$, $\text{Sn}_{0.9}\text{Fe}_{0.3}\text{B}_{0.4}\text{P}_{0.4}\text{Ca}_{0.1}\text{Rb}_{0.1}\text{O}_{2.95}$,

$\text{Sn}_{0.8}\text{Pb}_{0.2}\text{Ca}_{0.1}\text{P}_{0.9}\text{O}_{3.35}$, $\text{Sn}_{0.3}\text{germanium}_{0.7}\text{Ba}_{0.1}\text{P}_{0.9}\text{O}_{3.35}$, $\text{Sn}_{0.9}\text{Mn}_{0.1}\text{Mg}_{0.1}\text{P}_{0.9}\text{O}_{3.35}$,

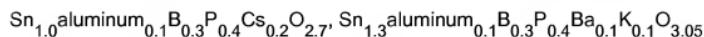
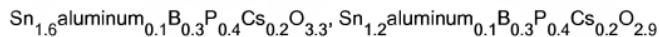
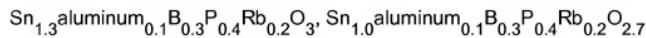
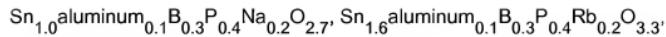
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[0029] $\text{Sn}_{1.6}\text{B}_{0.4}\text{P}_{0.4}\text{Ca}_{0.2}\text{O}_{3.4}$, $\text{Sn}_{1.3}\text{B}_{0.4}\text{P}_{0.4}\text{Ca}_{0.2}\text{O}_{3.1}$, $\text{Sn}_{1.6}\text{B}_{4}\text{P}_{0.4}\text{Ba}_{0.2}\text{O}_{3.4}$,

$\text{Sn}_{1.3}\text{B}_{0.4}\text{P}_{0.4}\text{Ba}_{0.2}\text{O}_{3.1}$, $\text{Sn}_{1.6}\text{B}_{0.4}\text{P}_{0.4}\text{Mg}_{0.2}\text{O}_{3.4}$, $\text{Sn}_{1.6}\text{aluminum}_{0.1}\text{B}_{0.3}\text{P}_{0.4}\text{Ca}_{0.2}\text{O}_{3.4}$, [0030]

$\text{Sn}_{1.3}\text{aluminum}_{0.1}\text{B}_{0.3}\text{P}_{0.4}\text{K}_{0.2}\text{O}_3$, $\text{Sn}_{1.0}\text{aluminum}_{0.1}\text{B}_{0.3}\text{P}_{0.4}\text{K}_{0.2}\text{O}_{2.7}$,

$\text{Sn}_{1.6}\text{aluminum}_{0.1}\text{B}_{0.3}\text{P}_{0.4}\text{Na}_{0.2}\text{O}_{3.3}$, $\text{Sn}_{1.3}\text{aluminum}_{0.1}\text{B}_{0.3}\text{P}_{0.4}\text{Na}_{0.2}\text{O}_3$,



[0031]The chemical formula of the compound produced by above-mentioned being calcinated is computable from the weight differences of the granular material before and behind calcination as inductively-coupled-plasma (ICP) emission spectrochemical analysis and a shortcut method as a measuring method.

[0032]50-700-mol% per negative pole material of the light metal insertion amount to the negative pole material of this invention is easy to be until it approximates it to the deposition potential of the light metal, but although it is desirable, it is especially desirable, for example.

[100-600-mol% of] Many the burst sizes are so preferred that there are to an insertion amount. The insertion method of a light metal has electrochemical and the preferred chemical and thermal method. The electrochemical process of the method of inserting electrochemically the light metal contained in positive active material or the method of inserting in direct electrochemistry from a light metal or its alloy is preferred. The chemical method has the method of making it react to mixing with a light metal, contact, or an organic metal, for example, butyl lithium etc. An electrochemical process and the chemical method are preferred. This especially light metal has lithium or a preferred lithium ion.

[0033]Various elements can be included in the negative pole material of this invention. For example, the dopant of lanthanoid series metal (Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg) and the various compounds (for example, compound of Sb, In, and Nb) which raise electron conductivity may also be included. 0-5-mol% of the quantity of the compound to add is desirable.

[0034]It can cover with an oxide with a chemical formula which is different from the positive active material used or a negative pole material in the positive active material of the oxide used by this invention, or the surface of a negative pole material. This scaling thing has a preferred oxide containing the compound which dissolves in acidity and alkalinity. The metallic oxide whose electron conductivity is still higher is preferred. For example, it is preferred to include dopants (for example, metal, a halogen, etc. in which valences differ in an oxide) in PbO_2 and Fe_2O_3 , SnO_2 , and In_2O_3 , ZnO(s) , or these oxides. They are SiO_2 , SnO_2 , and Fe_2O_3 , ZnO , and PbO especially preferably. As for the quantity of the metallic oxide used for these surface treatments, 0.1 to 10 % of the weight per this positive active material and negative pole material is preferred, especially its 0.2 to 5 % of the weight is preferred, and its 0.3 to 3 % of the weight is the most preferred. In addition, the surface of positive active material or a

negative pole material can be reformed. For example, processing by an esterification agent and processing the surface of a metallic oxide by processing, a conductive polymer, polyethylene oxide, etc. by a chelating agent is mentioned.

[0035]Although the transition metal oxide which can carry out insertion discharge of the lithium ion reversibly may be sufficient as the positive active material used by this invention, especially a lithium containing transition metal oxide is preferred. As desirable lithium containing transition metal oxide positive active material used by this invention, the oxide containing the lithium content Ti and V, Cr, Mn, Fe, Co, nickel, Cu, Mo, and W is raised. alkaline metals (the [of the periodic table] the [IA,] element of IIA) other than lithium -- and -- or aluminum, Ga, In, germanium, Sn, Pb, Sb, Bi, Si, P, B, etc. may be mixed. 0-30-mol% of a mixed amount is desirable to a transition metal. Rather than used by this invention as desirable lithium containing transition metal oxide positive active material, It is preferred to mix and compound so that the mole ratio of the sum total of a lithium compound/transition metal compound (at least one sort chosen from Ti, V, Cr, Mn, Fe, Co, nickel, Mo, and W with a transition metal here) may be set to 0.3-2.2. As lithium containing transition metal oxide positive active material desirable for using and solving by this invention, It is preferred to mix and compound so that the mole ratio of the sum total of a lithium compound/transition metal compound (at least one sort chosen from V, Cr, Mn, Fe, Co, and nickel with a transition metal here) may be set to 0.3-2.2. It is preferred that lithium containing transition metal oxide positive active material desirable for using and solving by this invention is Li_xQO_y (Q is mainly the transition metal in which a kind contains Co, Mn, nickel, V, and Fe at least here), $x=0.2-1.2$, and $y=1.4-3$. As Q, aluminum, Ga, In, germanium, Sn, Pb, Sb, Bi, Si, P, B, etc. may be mixed in addition to a transition metal. 0-30-mol% of a mixed amount is desirable to a transition metal.

[0036]Furthermore it is used by this invention, as desirable lithium contained metal oxide positive active material, Li_xCoO_2 , Li_xNiO_2 , Li_xMnO_2 , $Li_xCo_a\text{nickel}_{1-a}O_2$, $Li_zCo_bV_{1-b}O_z$, $Li_xCo_bFe_{1-b}O_2$, $Li_xMn_2O_4$, $Li_xMn_cCo_{2-c}O_4$, $Li_xMn_c\text{nickel}_{2-c}O_4$, $Li_xMn_{2-c}O_2$, $Li_xMn_cFe_{2-c}O_4$, $Li_xCo_bB_{1-b}O_2$, The mixture of $Li_xCo_bSi_{1-b}O_2$, and $Li_xMn_2O_4$ and MnO_2 , the mixture of $Li_{2x}MnO_3$ and MnO_2 , $Li_xMn_2O_4$, The mixture (it is $x=0.2-1.2$, $a=0.1$ to 0.9 , $b=0.8$ to 0.98 , $c=1.6-1.96$, and $z=2.01-5$ here) of $Li_{2x}MnO_3$ and MnO_2 can be raised. Furthermore it is used by this invention, as desirable lithium contained metal oxide positive active material, Li_xCoO_2 , Li_xNiO_2 , Li_xMnO_2 , $Li_xCo_a\text{nickel}_{1-a}O_2$, $Li_xCo_bV_{1-b}O_z$, $Li_xCo_bFe_{1-b}O_2$, $Li_xMn_2O_4$, $Li_xMn_cCo_{2-c}O_4$, $Li_xMn_c\text{nickel}_{2-c}O_4$, $Li_xMn_{2-c}O_2$, $Li_xMn_cFe_{2-c}O_4$ (it is $x=0.7-1.2$, $a=0.1$ to 0.9 , $b=0.8$ to 0.98 , $c=1.6-1.96$, and $z=2.01-2.3$ here) is raised. As most desirable lithium containing transition metal oxide positive active material used by this invention, Li_xCoO_2 , Li_xNiO_2 ,

Li_xMnO_2 , $\text{Li}_x\text{Co}_a\text{nickel}_{1-a}\text{O}_2$, $\text{Li}_x\text{Mn}_2\text{O}_4$ and $\text{Li}_x\text{Co}_b\text{V}_{1-b}\text{O}_z$ (it is $x = 0.7\text{-}1.2$, $a = 0.1$ to 0.9 , $b = 0.9$ to 0.98 , and $z = 2.02\text{-}2.3$ here) are raised. Here, the above-mentioned x value is a value before a charge-and-discharge start, and is fluctuated by charge and discharge.

[0037] Although positive active material is compoundable by the method and solution reaction which mix a lithium compound and a transition metal compound and are calcinated, especially its calcinating method is preferred. The calcination temperature used by this invention should just be a temperature which some mixed compounds which are used by this invention decompose and fuse, for example, its $250\text{-}2000$ ** is preferred, and its $350\text{-}1500$ ** is especially preferred. It is preferred to carry out temporary quenching at $250\text{-}900$ ** when calcinating. As firing time, 1 to 72 hours is 2 to 20 hours desirable still more preferably. Dry type or a wet type may be sufficient as the mixed method of a raw material. It may anneal at 200 ** - 900 ** after calcination. A calcination gas atmosphere in particular is not limited, but both an oxidizing atmosphere and reducing atmosphere can take it. For example, the gas which prepared the oxygen density in arbitrary proportion among the air or hydrogen, carbon monoxide, nitrogen, argon, helium, krypton, a xenon, carbon dioxide, etc. are mentioned.

[0038] The method of compounding when compounding the positive active material of this invention by making it react to a lithium metal, a lithium alloy, butyl lithium, and a transition metal oxide as a method of inserting a lithium ion in a transition metal oxide chemically is preferred. Although the mean grain size in particular of the positive active material used by this invention is not limited, 0.1-50 micrometers is preferred. Although not limited especially as specific surface area, $0.01\text{-}50\text{-m}^2/\text{g}$ is preferred at a BET adsorption method. As the pH of supernatant liquid when the positive active material 5g is melted in 100 ml of distilled water, 12 or less [7 or more] are preferred. In order to use predetermined grain size, the grinder and classifier which were known well are used. For example, a mortar, a ball mill, a vibration ball mill, a vibration mill, a satellite ball mill, a planetary ball mill, a turning air stream type jet mill, a screen, etc. are used. The positive active material obtained by calcination may be used after water, aqueous acids, an alkaline aqueous solution, and an organic solvent wash.

[0039] The combination of the negative pole material and positive active material which are used for this invention, The compound and Li_xCoO_2 which are preferably shown by a general formula (1), Li_xNiO_2 , $\text{Li}_x\text{Co}_a\text{nickel}_{1-a}\text{O}_2$, Li_xMnO_2 and $\text{Li}_x\text{Mn}_2\text{O}_4$. Or it is the combination of $\text{Li}_x\text{Co}_b\text{V}_{1-b}\text{O}_z$ (it is $x = 0.7\text{-}1.2$, $a = 0.1$ to 0.9 , $b = 0.9$ to 0.98 , and $z = 2.02\text{-}2.3$ here), The nonaqueous secondary battery which excelled [high capacity / high discharge voltage and] in the charge-discharge cycle characteristic can be obtained.

[0040] The equivalent of the lithium insertion to the negative pole material of this invention is 3-10 Eq, and determines the amount-used ratio with positive active material according to this equivalent. It is preferred to use [twice / 0.5 to / as many as this] for the amount-used ratio

based on this equivalent, applying it. A lithium supply source determines the amount of the positive active material used according to the lithium discharge equivalent of a negative pole material (for example, a lithium metal, an alloy, butyl lithium, etc.) except positive active material. It is preferred to use [twice / 0.5 to / as many as this] for the amount-used ratio based on this equivalent also at this time, applying it.

[0041]When inserting lithium in the negative electrode from lithium supply sources other than an anode beforehand, as a lithium supply source, it is preferred to use a lithium metal, and the foil and the metal powder of a lithium alloy (alloy of aluminum, aluminum-Mn, aluminum-Mg, aluminum-Sn, aluminum-In, aluminum-Cd, and lithium). These metallic foils may be located via the protective layer of direct or this invention on negative electrode mixture. You may make it located on a charge collector without negative electrode mixture. Foil may give an about 20-micrometer thin thing uniformly, and may arrange a thicker thing selectively. The thickness of foil can be decided to be the nature after cell formation from the quantity inserted in a negative electrode.

[0042]A conducting agent, a binder, a filler, etc. can be added in an electrode compound. In the constituted cell, if a conducting agent is a electron conductive material which does not cause a chemical change, it is [anything] good. Usually, natural graphite (flaky graphite, scaly graphite, earthy graphite, etc.), an artificial graphite, Conductive materials, such as carbon black, acetylene black, Ketchen black, carbon fiber, metal powder (copper, nickel, aluminum, silver, etc.) and a metal fiber, or a polyphenylene derivative, can be included as one sort or these mixtures. Especially concomitant use of black lead and acetylene black is preferred. As for the addition, 1 to 50 % of the weight is preferred, and its 2 to 30 % of the weight is especially preferred. In carbon or especially black lead, 2 to 15 % of the weight is preferred.

[0043]In a binder, usually Starch, polyvinyl alcohol, carboxymethyl cellulose, Hydroxypropylcellulose, regenerated cellulose, diacetyl cellulose, Polyvinylchloride, a polyvinyl pyrrolidone, tetrafluoroethylene, Polyvinylidene fluoride, polyethylene, polypropylene, an ethylene-propylene-diene terpolymer (EPDM), The polymer etc. which have polysaccharide, such as sulfonation EPDM, styrene butadiene rubber, polybutadiene, fluorocarbon rubber, and polyethylene oxide, thermoplastics, and rubber elasticity are used as one sort or these mixtures. When using the compound containing a functional group which reacts to lithium like polysaccharide, it is preferred to, add a compound like an isocyanate group for example, and to deactivate the functional group. As for the addition of the binder, 1 to 50 % of the weight is preferred, and its 2 to 30 % of the weight is especially preferred. In the constituted cell, a filler can be used anything, if it is the fibrous material which does not cause a chemical change. Usually, textiles, such as olefin system polymer, such as polypropylene and polyethylene, glass, and carbon, are used. Although the addition in particular of a filler is not limited, 0 to 30 % of the weight is preferred.

[0044]In using the negative pole material of this invention in a nonaqueous secondary battery system, the moisture powder mixture paste containing the compound of this invention is applied and dried on a charge collector, and it is preferred that pH of this moisture powder mixture paste is less than [5 or more] 10 and less than [further 6 or more] 9. It is preferred to keep the temperature of this moisture powder paste at not less than 5 ** less than 80 **, and to perform spreading of a up to [a charge collector] within seven days after preparation of a paste.

[0045]As a separator, it has the big degree of ion permeation, and has a predetermined mechanical strength, and material with insulating fine porosity or a crevice is used. For the improvement in safety, it is required to have a function which blockades the above-mentioned crevice above 80 **, raises resistance, and intercepts current. Not less than 90 ** 180 ** or less of blockade temperature of these crevices is not less than 110 ** 170 ** or less more preferably. How to make a crevice may be which a publicly known method, although it changes with materials. In the case of a porosity film, the shape of a hole is usually a round shape and an ellipse form, a size is 0.05 micrometer to 30 micrometers, and its 0.1 to 20 micrometers are preferred. It may be a hole of rod form or an infinite form like [at the time of making by the extending method and a phase separation method]. In the case of cloth, a crevice is an opening between textiles and it is dependent on how to make textile fabrics and a nonwoven fabric. It is 20% to 90%, the ratio, i.e., the porosity, to which these crevices close, and it is desirable. [35 to 80% of]

[0046]Not less than 5 micrometers 100 micrometers or less of separators of this invention are cloth, such as a not less than 10-micrometer film of 80 micrometers or less of fine porosity, textile fabrics, and a nonwoven fabric, more preferably. One in which that in which the separator of this invention contains an ethylene ingredient at least 20% of the weight is desirable especially preferred is included not less than 30%. As ingredients other than ethylene, propylene, a butene, a hexene, ethylene fluoride, VCM/PVC, vinyl acetate, and acetalization vinyl alcohol are raised, and propylene and especially ethylene fluoride are preferred. As for the film of fine porosity, what consists of polyethylene, ethylene propylene copolymerization polymer, or ethylene butene copolymerization polymer is preferred. What carried out the mixture solution of polyethylene, polypropylene and polyethylene, and the poly ethylene tetrafluoride, and made them is preferred. From 0.1 micrometer, a nonwoven fabric and textile fabrics are 5 micrometers, and the path of thread Polyethylene, What consists of ethylene propylene copolymerization polymer, ethylene butene-1 copolymerization polymer, ethylene methylbutene copolymerization polymer, ethylene methylpentene copolymerization polymer, polypropylene, and poly ethylene tetrafluoride fiber threads is preferred. These separators may be single materials or may be composite materials. Especially the thing that compounded the material of the gestalt in which what laminated two or more sorts of

microporous film into which an aperture, porosity, the blockade temperature of the hole, etc. were changed especially, microporous film, a nonwoven fabric and microporous film, and textile fabrics and a nonwoven fabric differ from paper etc. is preferred. The separator of this invention may contain the particles of inorganic substances, such as inorganic fibers, such as glass fiber and carbon fiber, a silicon dioxide, zeolite and alumina, and talc. What processed and carried out hydrophilization of an opening or the surface with the surface-active agent may be used.

[0047]As an electrolyte, as an organic solvent, propylene carbonate, ethylene carbonate, Butylene carbonate, dimethyl carbonate, diethyl carbonate, Gamma-butyrolactone, 1,2-dimethoxyethane, a tetrahydrofuran, 2-methyltetrahydrofuran, dimethyl sulfoxide, 1,3-dioxolane, A formamide, dimethylformamide, dioxolane, acetonitrile, Nitromethane, methyl formate, methyl acetate, methyl propionate, ethyl propionate, Trialkyl phosphate, trimethoxy methane, a dioxolane derivative, sulfolane, 3-methyl-2-oxazolidinone, a propylene carbonate derivative, The lithium salt which melts into the solvent which mixed at least one or more sorts of aprotic organic solvents, such as a tetrahydrofuran derivative, diethylether, and 1,3-propane Salton, and its solvent, For example, LiClO_4 , LiBF_4 , LiPF_6 , LiCF_3SO_3 , LiCF_3CO_2 , LiAsF_6 , LiSbF_6 , $\text{LiB}_{10}\text{Cl}_{10}$, low-grade aliphatic-carboxylic-acid lithium, LiAlCl_4 , It comprises one or more sorts of salts, such as LiCl , LiBr , LiI , chloroboranelithium, and 4 phenyl lithium borate. Into the mixed liquor of propylene carbonate or ethylene Cabot, 1 and 2-dimethoxyethane and/, or diethyl carbonate, LiCF_3SO_3 especially, The electrolysis solution containing LiClO_4 , LiBF_4 and/, or LiPF_6 is preferred. Especially the electrolysis solution that contains LiBF_4 and/, or LiPF_6 in the mixed liquor of diethyl carbonate with ethylene Cabot is preferred. although the quantity in particular that adds these electrolytes in a cell is not limited -- positive active material, the quantity of a negative pole material, and the size of a cell -- **** for initial complements -- things are made. As for the concentration of a supporting electrolyte, 0.2-3 mol per l. of electrolysis solution is preferred.

[0048]The following solid electrolytes can also be used besides an electrolysis solution. It is divided into an inorganic solid electrolyte and an organic solid electrolyte as a solid electrolyte. The nitride of Li, the halogenide, the oxygen acid salt, etc. are well known by the inorganic solid electrolyte. Li_3N , LiI , Li_5Ni_2 especially, $\text{Li}_3\text{N-LiI-LiOH}$, LiSiO_4 , and $\text{LiSiO}_4\text{-LiI-LiOH}$, $x\text{Li}_3\text{PO}_4\text{-(1-x)}\text{Li}_4\text{SiO}_4$, Li_2SiS_3 , a phosphorus sulfide compound, etc. are effective. The polymer which contains a polyethylene oxide derivative or this derivative in an organic solid electrolyte, Polymer containing a polypropylene oxide derivative or this derivative, polymer containing an ionic dissociation group, polymer containing an ionic dissociation group, and the mixture of the above-mentioned aprotic electrolysis solution and phosphoric ester polymer are

effective. There is also the method of adding polyacrylonitrile to an electrolysis solution. How to use together inorganic matter and an organic solid electrolyte is also known.

[0049]As a separator, it has the big degree of ion permeation, and has a predetermined mechanical strength, and an insulating thin film is used. The sheet and nonwoven fabric which were built from organic solvent-proof nature and hydrophobicity from olefin system polymer, glass fiber, or polyethylene, such as poly pre pyrene, etc. are used. The range for which the aperture of a separator is generally used as an object for cells is used. For example, 0.01-10 micrometers is used. Generally the thickness of SEPARATA is used in the range for cells. For example, 5-300 micrometers is used. Adding to an electrolyte the compound shown below in order to improve discharge and a charging and discharging characteristic is known. For example, pyridine, triethyl phosphite, triethanolamine, Cyclic ether, ethylenediamine, n-glyme, hexalin acid TORIAMIDO, A nitrobenzene derivative, sulfur, a quinonimine dye, N-substitution oxazolidinone and N,N'-substitution imidazolidinone, Ethylene glycol dialkyl ether, quarternary ammonium salt, polyethylene glycols, Pyrrole, 2-methoxyethanol, AlCl_3 , the monomer of a conductive polymer electrode active material, The triethylenephosphoramide, trialkylphosphine, morpholine, An aryl compound and hexamethylphosphoric triamide with a carbonyl group, 4-alkyl morpholine and the bicyclic third class amine, oil (JP,62-287,580,A), the fourth class phosphonium salt, the third class sulfonium salt, etc. are mentioned.

[0050]In order to make an electrolysis solution into incombustibility, a halogen-containing solvent, for example, a carbon tetrachloride, and 3 fluoridation ethylene chloride can be included in an electrolysis solution. In order to give fitness to high temperature preservation, carbon dioxide can be included in an electrolysis solution. An electrolysis solution or an electrolyte can be included in the mixture of an anode or a negative electrode. For example, the method of including said ion conductivity polymer, nitromethane, and an electrolysis solution is known.

[0051]It is [anything] good if it is an electronic conductor which does not cause a chemical change in the constituted cell as a charge collector of positive and negative poles. For example, the thing which made the surface of aluminum or stainless steel else [, such as stainless steel, nickel, aluminum, titanium, and carbon,] process carbon, nickel, titanium, or silver as a material is used for an anode. In particular, aluminum or an aluminum alloy is preferred. The thing which made the surface of copper or stainless steel else [, such as stainless steel, nickel, copper, titanium, aluminum, and carbon] process carbon, nickel, titanium, or silver, an aluminum-Cd alloy, etc. are used for a negative electrode as a material. In particular, copper or a copper alloy is preferred. Oxidizing the surface of such materials is also used. It is desirable to attach unevenness to a collector surface by a surface treatment. As for shape, a sheet, the thing netted and punched, a film, the Russ object besides foil, a porous body, foam, the Plastic solid of a textiles group, etc. are used. Although thickness in particular

is not limited, a 1-500-micrometer thing is used.

[0052]The shape of a cell can apply coin, a button, a sheet, a cylinder, flatness, an angle, etc. to all. At the time of coin or a button, the shape of a cell is compressed into the shape of a pellet and, as for the mixture of positive active material or a negative pole material, is mainly used. The thickness and the diameter of the pellet are decided with the size of a cell. When the shape of a cell is a sheet, a cylinder, and an angle, on a charge collector, the mixture of positive active material or a negative pole material is applied (coat) dried and compressed, and is mainly used. A general method can be used for a coating method. For example, the reverse roll method, the Dailekh trawl method, the braid method, the knife method, the extrusion method, the curtain method, the photogravure method, the bar method, a dip method, and the squeeze method can be mentioned. The braid method, the knife method, and the extrusion method are preferred also in it. As for spreading, it is preferred to carry out the speed for 0.1-100-m/. Under the present circumstances, according to the solution physical properties of a mixture, and drying property, the surface state of a good coating layer can be acquired by selecting the above-mentioned coating method. The time of one side [every] ** or double-sided coincidence may be sufficient as spreading. Continuation, an intermission, or a stripe may be sufficient as spreading. Although the thickness, length, and width of the coating layer are decided with the size of a cell, the thickness of the coating layer of one side is in the compressed state after dry, and especially its 1-2000 micrometers are preferred.

[0053]The method generally adopted can be used as a pellet, or desiccation of a sheet or a dehydration method. In particular, it is preferred independent, to combine and to use a hot wind, a vacuum, infrared rays, far-infrared rays, an electron beam, and a damp wind. The temperature of the range of 80-350 ** is preferred, and is especially preferred. [of the range which is 100-250 **] 2000 ppm or less of water content are preferred by the whole cell, and it is preferred to use 500 ppm or less in positive electrode mixture, negative electrode mixture, or an electrolyte, respectively in respect of cycle nature. Although the method generally adopted can be used for a pellet or the method of pressing a sheet, they are especially preferred. [of a die-press method or the calendar pressing method] Although press pressure in particular is not limited, its 0.2 - 3 t/cm² is preferred. As for the pressing speed of the calendar pressing method, the amount of 0.1-50-m/s is desirable, and room temperature -200 ** of press temperature is preferred. As for the ratio of negative electrode sheet width to a positive electrode sheet, 0.9-1.1 are preferred, and 0.95-especially 1.0 are preferred. Since the content ratio of positive active material and a negative pole material changes with a compound kind or mixture formulas, it cannot be limited, but it can be set as the optimal value in the viewpoint of capacity, cycle nature, and safety.

[0054]After rolling or folding those sheets after piling up via this mixture sheet and a separator, inserting them in a can and electrically connecting a sheet with a can, they pour in an

electrolysis solution and form a battery can using an obturation board. At this time, a safety valve can be used as an obturation board. It may be equipped with various safety elements known from the former besides a safety valve. For example, a fuse, bimetal, a PTC element, etc. are used as an overcurrent-protection element. The method of making a cut in a battery can other than a safety valve, the gasket crack method, the obturation board crack method, or cutting process with a lead board can be used as a measure against the internal pressure rise of a battery can. The protection circuit which built the surcharge and the measure against overdischarge into the battery charger may be made to provide, or it may be made to connect independently. The method which intercepts current by the rise of inter cell pressure can be provided as a measure against overcharge. At this time, the compound which increases internal pressure can be included in a mixture or an electrolyte. As an example of the compound used in order to increase internal pressure, carbonate, such as Li_2CO_3 , LiHCO_3 , Na_2CO_3 , NaHCO_3 , CaCO_3 , and MgCO_3 , etc. can be mentioned.

[0055] Metal and an alloy with electrical conductivity can be used for a can or a lead board. For example, metal or those alloys, such as iron, nickel, titanium, chromium, molybdenum, copper, and aluminum, are used. A publicly known method (electric welding of an example, a direct current, or exchange, laser welding, ultrasonic welding) can be used for the welding process of a cap, a can, a sheet, and a lead board. The compound and mixture which are known from the former, such as asphalt, can be used for the sealing compound for obturation.

[0056] Although not limited to the use in particular of the nonaqueous secondary battery of this invention, when it carries in electronic equipment, for example, A color notebook computer, monochrome notebook computer, a pen input personal computer, a pocket (palm top) personal computer, A note type word processor, a pocket word processor, an Electronic Book player, a cellular phone, A cordless phone cordless handset, a pager, a handy terminal, portable fax, A portable copy, a portable printer, a headphone stereo, a video movie, A liquid crystal television, a handy cleaner, portable CD, a mini disc, an electric shaver, an electronic translating machine, a car telephone, a transceiver, a power tool, an electronic notebook, a calculator, memory card, a tape recorder, radio, a backup power supply, memory card, etc. are mentioned. In addition, as a noncommercial use, a car, an electric motor, a motor, a light, a toy, a game machine machine, a load conditioner, an iron, a clock, a stroboscope, a camera, medical equipment (a pacemaker, hearing aid, and a shoulder are also ****s etc.), etc. are mentioned. It can use as the various objects for munitions, and an object for the universes. It is also combinable with a solar cell.

[0057]

[Example] Although an example is raised to below and this invention is explained in more detail, unless the main point of an invention is exceeded, this invention is not limited to an example.

[0058]Dry blending of 13.5 g of synthetic example-1 tin protoxide, the silicon dioxide 3.6g, the magnesium oxide 0.64g, and 0.69 g of the oxidation boron was carried out, it put into the crucible made from alumina, and temperature up was carried out to 1000 ** by a part for bottom 15 **/of argon atmosphere. After calcinating at 1200 ** for 10 hours, the temperature was lowered even to the room temperature by a part for 10 **/, it took out from the firing furnace, coarse grinding of this was carried out, the jet mill ground further, and $\text{SnSi}_{0.6}\text{Mg}_{0.2}\text{B}_{0.2}\text{O}_{2.7}$ (compound 1-A) with a mean particle diameter of 4.5 micrometers was obtained. It is a thing which has a broadcloth peak which has the peak near 28 degree with 2theta value in the X-ray diffraction method using CuK alpha rays, and the crystalline diffraction line was not looked at by not less than 40 degrees 70 degrees or less with 2theta value.

[0059]In the similar way, the raw material of the amount of stoichiometries was mixed, calcinated and ground, respectively, and the following compound was obtained.

$\text{SnSi}_{0.8}\text{Mg}_{0.2}\text{O}_{2.8}$ (1-B), $\text{SnSi}_{0.6}\text{aluminum}_{0.2}\text{Mg}_{0.2}\text{O}_{2.7}$ (1-C), $\text{SnSi}_{0.6}\text{P}_{0.2}\text{Mg}_{0.2}\text{O}_{2.9}$ (1-D),

$\text{SnSi}_{0.6}\text{aluminum}_{0.1}\text{B}_{0.2}\text{Mg}_{0.1}\text{O}_{2.75}$ (1-E), $\text{SnSi}_{0.5}\text{P}_{0.1}\text{B}_{0.1}\text{Mg}_{0.3}\text{O}_{2.7}$ (1-F).

[0060]As example-1 negative pole material, compound 1-A compounded by synthetic example-1 is used, It was mixed at a rate of 6 % of the weight of scaly graphite 88% of the weight, and also 1 % of the weight of carboxymethyl cellulose and 1 % of the weight of lithium acetate were added for the water dispersed matter of poly fluoridation kinky thread NIDEN 4% of the weight as a binder, water was kneaded as a medium, and the slurry was produced. This slurry was applied to both sides of 18-micrometer-thick copper foil by the extrusion method, and the negative electrode a was made. On the negative electrode a, it mixed at 97 % of the weight of alpha-aluminum O_3 (mean particle diameter of 1 micrometer), and a rate of 3 % of the weight of carboxymethyl cellulose, and the negative electrode b applied and created what kneaded water as a medium and slurred it. carrying out compression molding of these negative electrodes, a, and the b with an after-desiccation calendar pressing machine, and cutting to predetermined width and length -- band-like each -- a negative electrode sheet, a, and b were produced. Negative electrode sheet a was 78 micrometers, and negative electrode sheet b of the thickness of the negative electrode sheet was 100 micrometers. As a positive electrode material, LiCoO_2 87 % of the weight, 6 % of the weight of scaly graphite, 3 % of the weight of polytetrafluoroethylene water dispersed matters and 1 % of the weight of sodium polyacrylate were further added as a binder, 3 % of the weight of acetylene black applied to both sides of 20-micrometer-thick aluminium foil the slurry produced by kneading water as a medium by the same method as the above, and the anode a was made. On the anode a, it mixed at 97 % of the weight of alpha-aluminum O_3 (mean particle diameter of 1 micrometer),

and a rate of 3 % of the weight of carboxymethyl cellulose, and the anode b applied and created what kneaded water as a medium and slurred it. These anodes, a, and b were dried, pressed and cut, and a positive electrode sheet, a, and b were made. Positive electrode sheet a was 250 micrometers, and positive electrode sheet b of the thickness of the positive electrode sheet was 265 micrometers. Negative electrode sheet a, positive electrode sheet a, and negative electrode sheet b and positive electrode sheet b were combined, and the cell A (for comparison) and the cell B (this invention) were made by the method described below. After [a negative electrode sheet and a positive electrode sheet] carrying out spot welding of the lead board of nickel and aluminum to an end, respectively, drying desiccation was carried out in dry air not more than dew point-40 ** for 150 ** 2 hours. It laminated in order of the dried [drying] positive electrode sheet (8) fine porosity polypropylene film separator (Celgard 2400), the negative electrode sheet (9) dried [drying], and the separator (10), this was involved in, and it wound spirally by the opportunity.

[0061]It stored to the iron closed-end cylindrical battery can (11) which serves this winding body as a negative pole terminal and which performed the nickel plate. 1L per LiPF₆ and LiBF₄ were poured into 0.95, respectively, 0.05 mol was contained and the electrolyte in which a solvent consists of ethylene carbonate and diethyl carbonate 2:8 capacity mixed liquor was poured into the battery can. the battery lid (12) which has a positive pole terminal -- a gasket (13) -- passing -- the cylindrical cell was produced in total. The positive pole terminal (12) connected beforehand the positive electrode sheet (8) and the battery can (11) with the negative electrode sheet (9) with the lead terminal. The section of the cylindrical cell was shown in drawing 1. (14) is a safety valve. It created the cell A (for comparison), and the ten cells B (this invention) at a time, respectively, and after charging to 4.15V by 1 mA/cm², they were saved for three weeks at 60 **. The open circuit voltage of each cell was measured three weeks afterward, and the following result was obtained.

Cell number Cell A (comparison cell) Cell B (cell of this invention)

***** Open circuit voltage 1 0.92 4.12. 2 1.02 4.10 3 1.00 4.08 4 0.78 4.09 5 0.98 4.11 6 1.12 4.13 7 1.03 4.11 8 0.91 4.08 9 0.81 4.09 10 0.54 From the result of 4.11 or more. The cell of this invention has few voltage drops under preservation clearly, and it turns out that the performance is stable.

[0062]It produced the 300 same cells as the cells A and B of example-2 Example 1 at a time, respectively, and charged to 4.15V. When asked for the number of the cell with faulty charge, by the cell A for comparison, by the cell B of six pieces and this invention, it is zero piece and it turned out that the inferior-goods incidence rate is improved clearly.

[0063]When 1-B to 1-F was used and the same experiment as example-1 was conducted instead of negative pole material 1-A used by example-3 example-1, the almost same result as example-1 was obtained.

The cell C was made combining negative electrode sheet b and positive electrode sheet a of example-4 example-1. The cell D was made combining positive electrode sheet c and negative electrode sheet a which changed the thickness of the protective layer and were made into 280 micrometers of sheet thickness instead of. [positive electrode sheet b] When the same experiment as example-1 was conducted using these cells C and D, it turned out that the performance of the voltage drop after saving at the cell B said appearance is stable few. However, open circuit voltage was falling more slightly [C and D] than the cell B.

On the negative electrode a of example-5 example-1, it mixed at a rate of 94 % of the weight of alpha-aluminum O_3 (mean particle diameter of 1 micrometer), 3 % of the weight of scaly graphite, and 3 % of the weight of carboxymethyl cellulose, and what applied and produced what kneaded water as a medium and slurred it was used as the negative electrode c. The cell B and the cell produced similarly were set to E, respectively except using c for a negative electrode sheet. When the same experiment as example-1 was conducted using the cell E, the almost same result as example-1 was obtained.

On the negative electrode a of example-6 example-1, 94.5 % of the weight of alpha-aluminum O_3 (mean particle diameter of 1 micrometer), It mixed at a rate of 4.5 % of the weight of polyvinylidene fluorides, and 1 % of the weight of carboxymethyl cellulose, and what applied and produced what kneaded water as a medium and slurred it was used as the negative electrode d. The cell B and the cell produced similarly were set to F except using d for a negative electrode sheet. When it produced ten the cells B, the cells E of example-5, and the cells F of example-1 at a time, respectively and charged by 4.15-2.8V, the service capacity in 5 mA/cm^2 and the service capacity in 1 mA/cm^2 were measured, and the following result was obtained. The rate when capacity of the cell B was made into 100% showed the service capacity in front.

Service capacity of the service capacity / 1 mA/cm^2 of 5 mA/cm^2 Cell B cell E cell F 1 88 89 81 2 87 89 823 90 89 82 4 88 90 82 5 89 89 81 6. 88 90 82 7 88 88 80 8 89 88 82 9 88 89 82 10 88 89 82 Service capacity average of 1 mA/cm^2 100 101 From the result of 89 or more. The cell of this invention has clearly large capacity, and it turns out that it excels in the service capacity of the service capacity / 1 mA/cm^2 of 5 mA/cm^2 .

On the negative electrode a of example-7 example-1, 93 % of the weight of alpha-aluminum O_3 (mean particle diameter of 1 micrometer), It mixed at a rate of 3 % of the weight of scaly graphite, 3 % of the weight of polyvinylidene fluorides, and 1 % of the weight of carboxymethyl cellulose, and what applied and produced what kneaded water as a medium and slurred it was used as the negative electrode d. Only coverage was reduced by the same method as the anode a of example-1, it was considered as the 225-micrometer-thick anode, and what

attached the same protective layer as the anode b to this was used as the anode d. On negative electrode sheet [of example-5] c, and negative electrode sheet d, a 120 mg [perg of negative pole material] lithium metal was made into the shape of a strip of paper, and was stuck, and the cell B and the cell produced similarly were used as the cells G and H, respectively except combining positive electrode sheet d. It produced ten of these at a time, respectively, the same examination as example-6 was done, and the following result was obtained. The rate when capacity of the cell G was made into 100% showed the service capacity in front.

5 mA/cm ² の放電容量 / 1 mA/cm ² の放電容量		
	電池G	電池H
1	8 8	8 0
2	8 9	8 1
3	8 8	8 0
4	8 8	7 9
5	8 9	7 7
6	8 9	7 8
7	8 8	7 8
8	8 8	8 0
9	9 0	7 9
10	8 9	8 0
1 mA/cm ² の放電容量平均	1 0 0	7 5

The cell of this invention has clearly large capacity, and the above result shows excelling in the service capacity of the service capacity / 1 mA/cm² of 5 mA/cm².

[0064]

[Effect of the Invention]The anode and negative electrode which include for lithium the material in which occlusion discharge is possible reversibly like this invention, By giving at least one layer of protective layers which become a negative electrode and/or an anode from a particle and water-soluble polymer in the nonaqueous electrolyte containing lithium salt and the nonaqueous secondary battery which comprises a separator, A nonaqueous secondary battery with preservation stability can be stably made from high discharge operating potential and big service capacity.

[Translation done.]